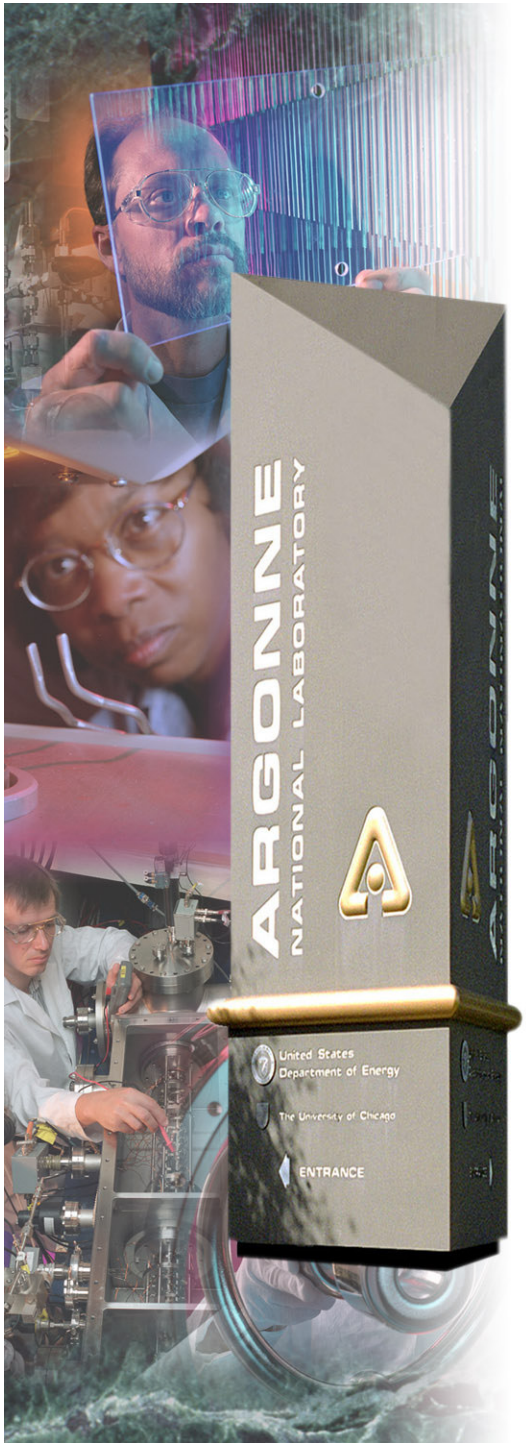

DFT-Based Nanostructure Investigation

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Office of Science
U.S. Department of Energy

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Office of Science Laboratory
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Acknowledgment

- **Collaborators:**

  - Mihai Anitescu – ANL, Math. and Comp. Science Division
  - Dan Negrut – ANL, Math. and Comp. Science Division

Overview

- Motivation
- Background information
- Proposed method
- Structure of the code
- Results and discussions

Motivation

- **Electronic structure of materials undergoes drastic changes when dimensions reduced to the nanoscale**
  - high density of surfaces and interfaces relative to volume
- **New regimes of physical, mechanical, and chemical behavior not observed in bulk materials**
- **Nanoscale oxide structures:**
  - Chemical reactivity
  - Magnetic properties
  - Charge transport
  - Optical properties

Important Quantities

- **TWO quantities are sought:**
  - Ground State Energy $\mathcal{E}_0$
  - Ground State Electron Density $\rho(\mathbf{r})$

- **Both obtainable if Schrödinger's equation is solved for the Wave Function**

$$\mathcal{H}\Psi = \mathcal{E}\Psi$$

$$\Psi(\mathbf{r}_1, \ldots, \mathbf{r}_N)$$

$$\mathcal{H} = -\sum_{i=1}^{N} \frac{1}{2}\nabla_i^2 - \sum_{i=1}^{N}\sum_{A=1}^{M} \frac{Z_A}{||\mathbf{r}_i - \mathbf{R}_A||} + \sum_{i=1}^{N}\sum_{j=i+1}^{N} \frac{1}{||\mathbf{r}_i - \mathbf{r}_j||}$$

Solving Schrödinger's Equation

- **Hartree-Fock approaches, and related methods**
  - Scale like N^4, or for more accurate computation can become as intensive as N^8 (perturbation theory)
  - For 80 atoms of Aluminum:

$$N \approx 1000 \Rightarrow 10^{24} \text{ operations}$$

- **Density Functional Theory (DFT) emerged as a more viable alternative**
  - Hohenberg-Kohn: the electron density uniquely defines the wave function

- **Represent then everything in terms of the electron density**
  - Replace wave function as unknown (dependency on 3N variables), with electron density function as unknown (dependency on 3 variables)
  - DFT scales like N^3 , produces good approximation for $\rho(\mathbf{r})$

DFT approach

- **Oldest energy functional due to Fermi**
  - Later improved by Thomas, and then Dirac

$$E_e\left[\rho, \{\mathbf{R}_A\}\right] = E_{ne}\left[\rho, \{\mathbf{R}_A\}\right] + J\left[\rho\right] + K\left[\rho\right] + T\left[\rho\right]$$

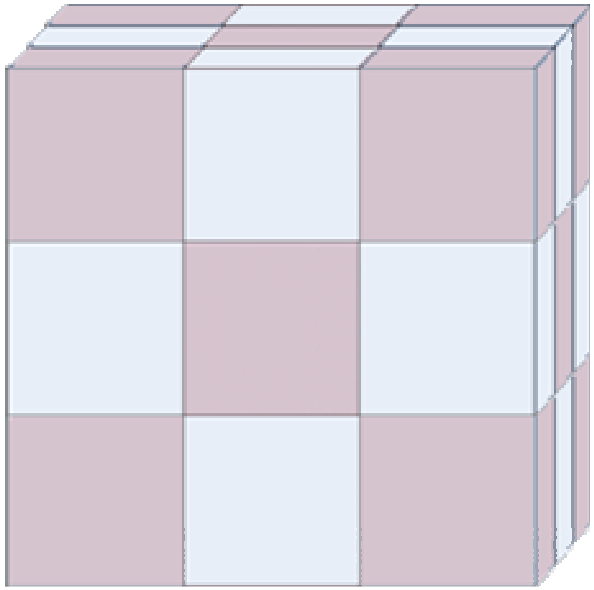
$$\begin{aligned}
E_{ne}\left[\rho, \{\mathbf{R}_A\}\right] &= -\sum_{A=1}^{M} \int \frac{Z_A\, \rho(\mathbf{r})}{\|\mathbf{R}_A - \mathbf{r}\|}\, \mathrm{d}\mathbf{r} \\
J\left[\rho\right] &= \frac{1}{2} \int\int \frac{\rho(\mathbf{r})\, \rho(\mathbf{r}')}{\|\mathbf{r} - \mathbf{r}'\|}\, \mathrm{d}\mathbf{r}\, \mathrm{d}\mathbf{r}' \\
T\left[\rho\right] &= C_F \int \rho^{\frac{5}{3}}(\mathbf{r})\, \mathrm{d}\mathbf{r} \\
K\left[\rho\right] &= -C_x \int \rho^{\frac{4}{3}}(\mathbf{r})\, \mathrm{d}\mathbf{r}
\end{aligned}$$

http://www-unix.mcs.anl.gov/~reconstruction/

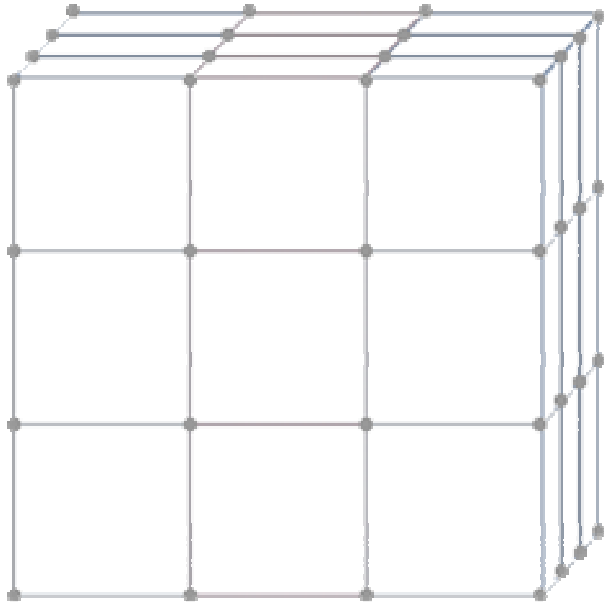
RECON

- **TWO STEPS**

Electronic Problem

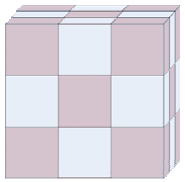


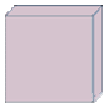
Ionic Problem



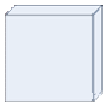
Electronic Problem

- **Electronic Problem**

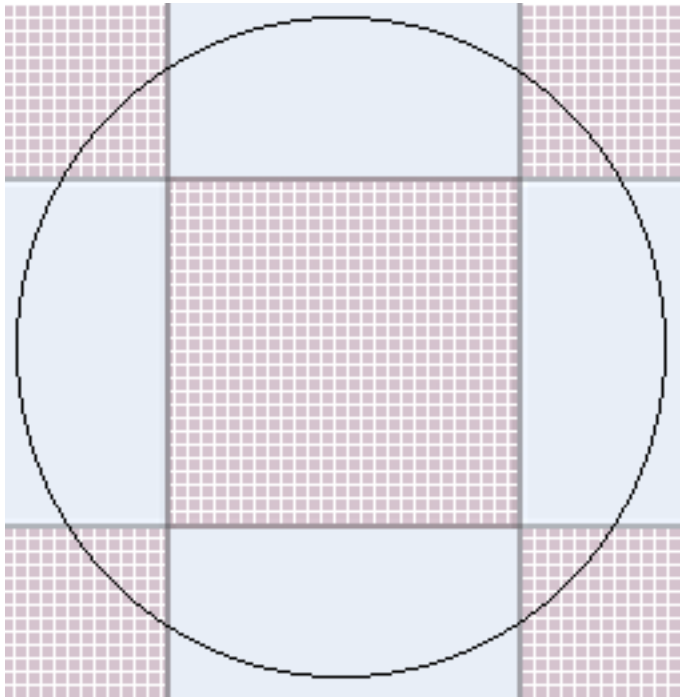




Generic



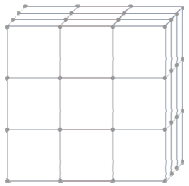
Reconstruction

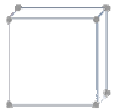


- 3D interpolation
- Support deformation through mapping

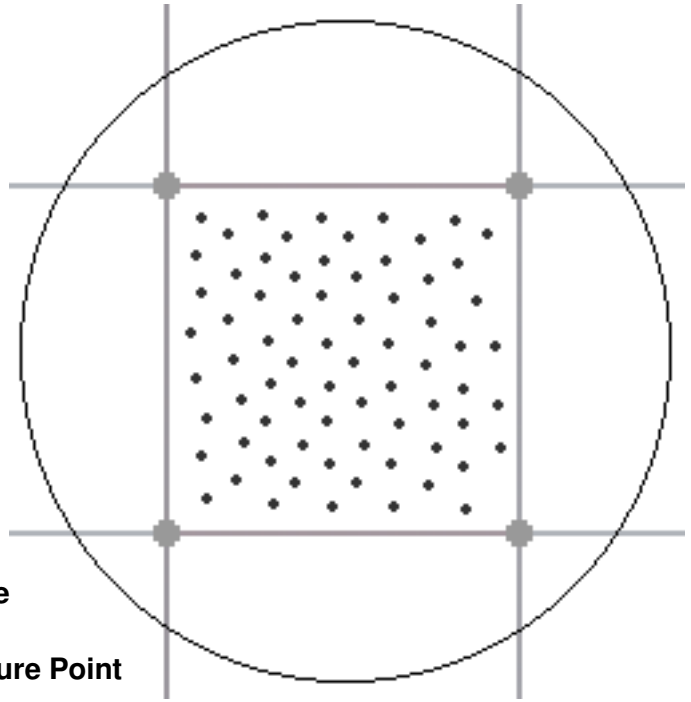
Electronic Problem

- **Ionic Problem**





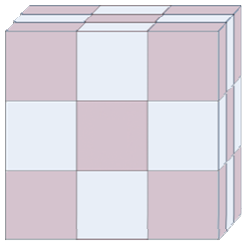
Atomic Control Volume (ACV)



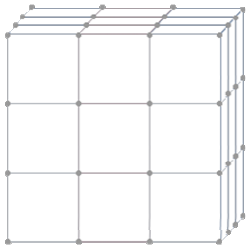
- Use only a subset of nuclei to impose the equilibrium conditions
- Follows the quasi-continuum framework

RECON

Electronic Problem



Ionic Problem



Electronic density

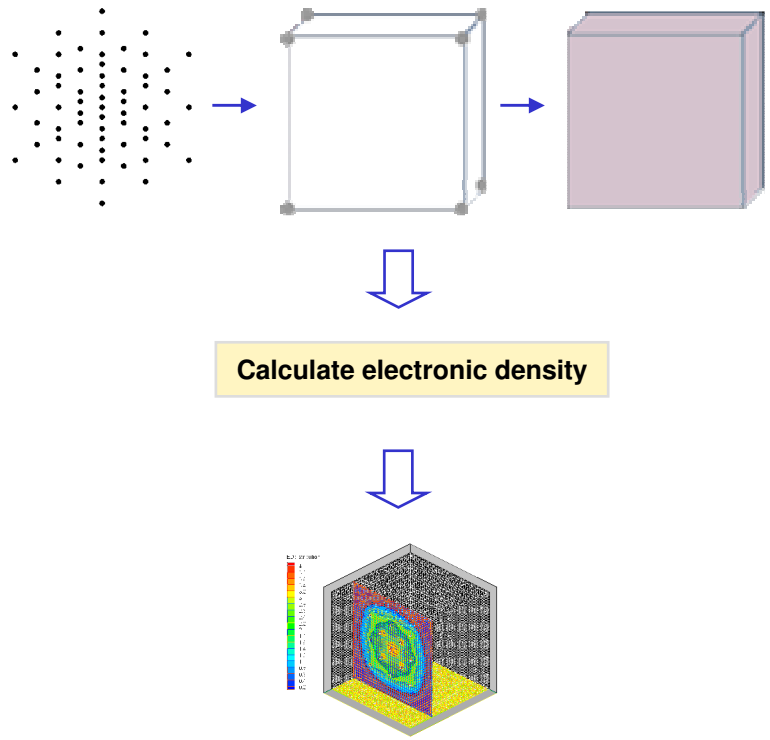
Positions of nuclei

Long Term Goal

Structure of RECON

Currently Implemented

- **Four stages:**
  - Preprocessing
  - Electronic Problem
  - Ionic Problem
  - Post processing

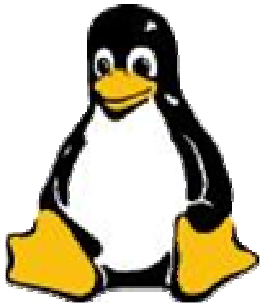


Running RECON – using TAO

- **Linux**

  Software needed

  - TAO
  - PETSc
  - MPICH2



- **Windows**

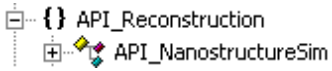
  Extra software needed

  - Cygwin

http://www-unix.mcs.anl.gov/~nano/

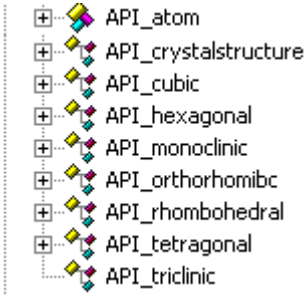
API Interface for RECON

- **API_NanostructureSim**



  - Size of electronic mesh
  - Number of electronic density cells in x-, y- and z-directions
  - Collection of atoms in the nanostructure

- **API_crystalstructure**

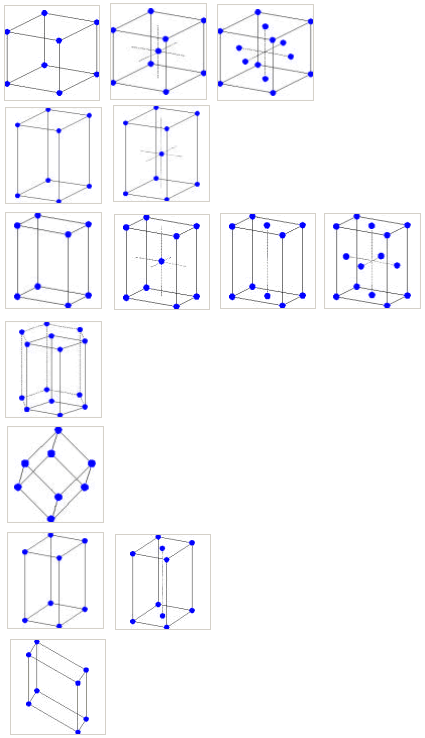


  - Supports bravais lattices

Bravais Lattices

- **Obey the following criteria**
  - unit cell is the repeating unit in the crystal
  - opposite faces of a unit cell are parallel
  - edge of the unit cell connects equivalent points

- **Seven crystal systems**
  - Cubic [P I F]
  - Tetragonal [P I]
  - Orthorhombic [P I C F]
  - Hexagonal
  - Rhombohedral
  - Monoclinic [P C]
  - Triclinic



Bravais Lattices

- **Convention**

a = is the magnitude of a_1 $\quad$ α = angle between a_2 and a_3

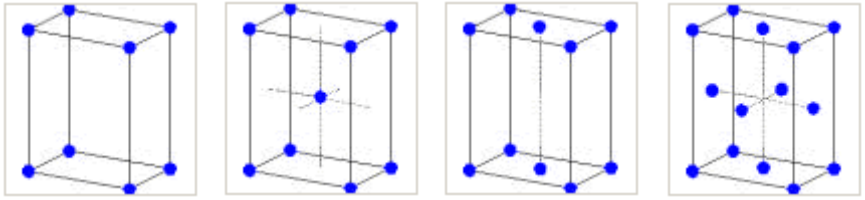
b = is the magnitude of a_2 $\quad$ β = angle between a_1 and a_3

c = is the magnitude of a_3 $\quad$ γ = angle between a_1 and a_2

- **3 primitive translation vectors** a_1, a_2, a_3

$$R_n = n_1 a_1 + n_2 a_2 + n_3 a_3$$

- Orthorhombic P I C F



Conditions

$a \neq b \neq c$

$\alpha = \beta = \gamma = 90^o$

$$a_1 = \begin{bmatrix} a \\ 0 \\ 0 \end{bmatrix} \quad a_2 = \begin{bmatrix} 0 \\ b \\ 0 \end{bmatrix} \quad a_3 = \begin{bmatrix} 0 \\ 0 \\ c \end{bmatrix}$$

$$a_1 = \frac{1}{2}\begin{bmatrix} a \\ -b \\ c \end{bmatrix} \quad a_2 = \frac{1}{2}\begin{bmatrix} a \\ b \\ -c \end{bmatrix} \quad a_3 = \frac{1}{2}\begin{bmatrix} -a \\ b \\ c \end{bmatrix}$$

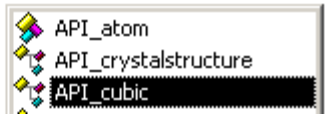
$$a_1 = \frac{1}{2}\begin{bmatrix} a \\ -b \\ 0 \end{bmatrix} \quad a_2 = \frac{1}{2}\begin{bmatrix} a \\ b \\ 0 \end{bmatrix} \quad a_3 = \begin{bmatrix} 0 \\ 0 \\ c \end{bmatrix}$$

$$a_1 = \frac{1}{2}\begin{bmatrix} a \\ 0 \\ c \end{bmatrix} \quad a_2 = \frac{1}{2}\begin{bmatrix} a \\ b \\ 0 \end{bmatrix} \quad a_3 = \frac{1}{2}\begin{bmatrix} 0 \\ b \\ c \end{bmatrix}$$

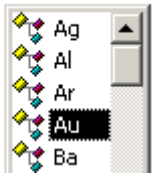
Example using the API Interface

- **Crystal structure**

```
//initialize cubic crystal structure
API_Reconstruction::
```




```
element::
```




```
API_Reconstruction::API_cubic* cubic = new API_Reconstruction::API_cubic(
```

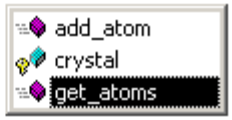
API_cubic (**int atomic_number**, char t, double _a, int unit_cells_x, int unit_cells_y, int unit_cells_z)

- **Nanostructure simulation model**

```
//define API_atoms and custom ACV
API_Reconstruction::API_NanostructureSim* sim = new API_Reconstruction::API_NanostructureSim(
```

API_NanostructureSim (**double h**, int ed_xcells, int ed_ycells, int ed_zcells, const std::vector<API_atom> &atoms, std::string tec_out = "tecplot_out")

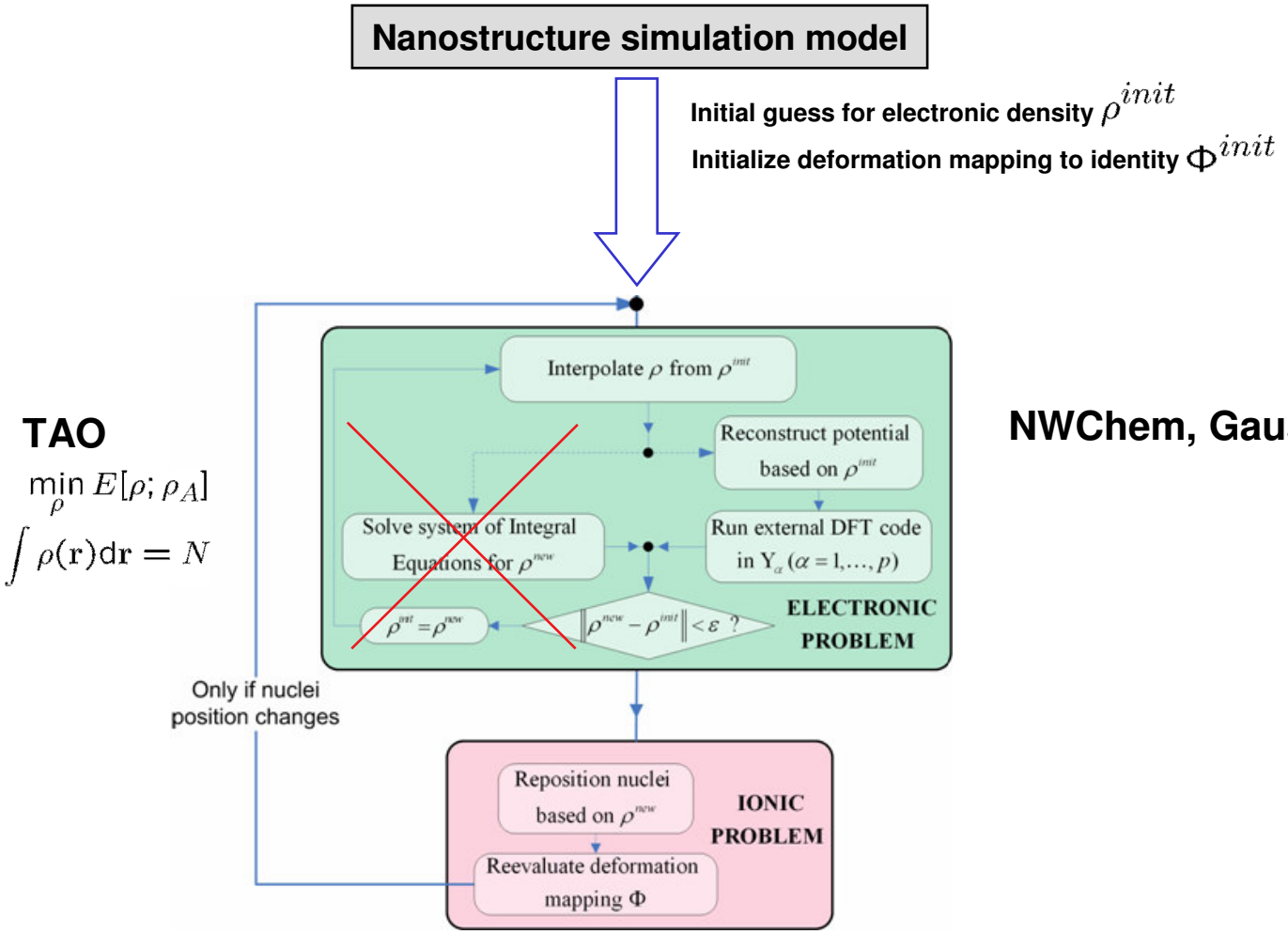
```
crystalstructure->
```



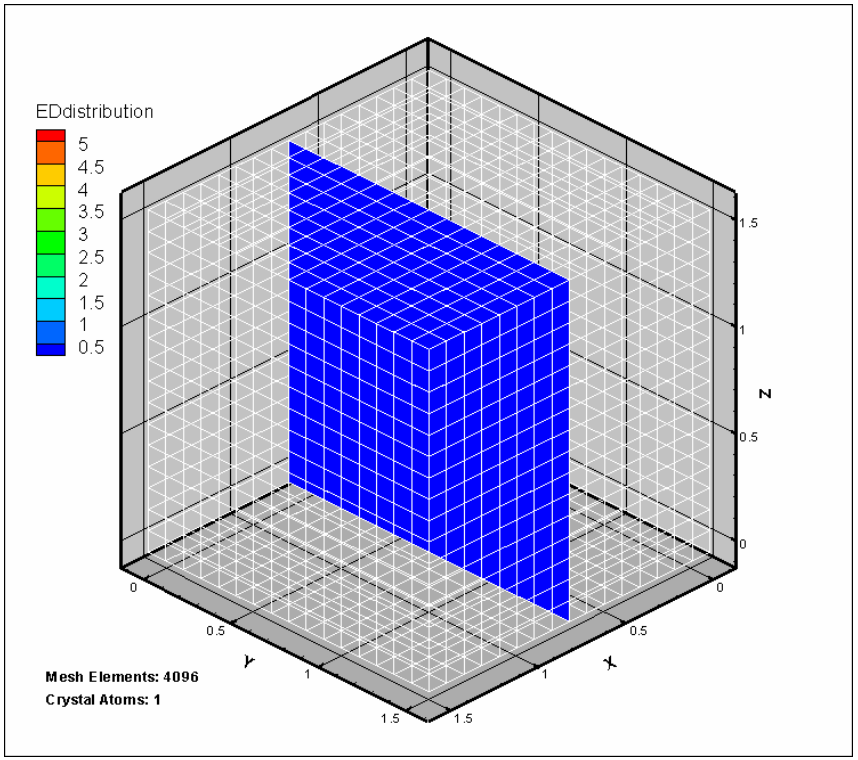
- **Interface to third party optimization software**

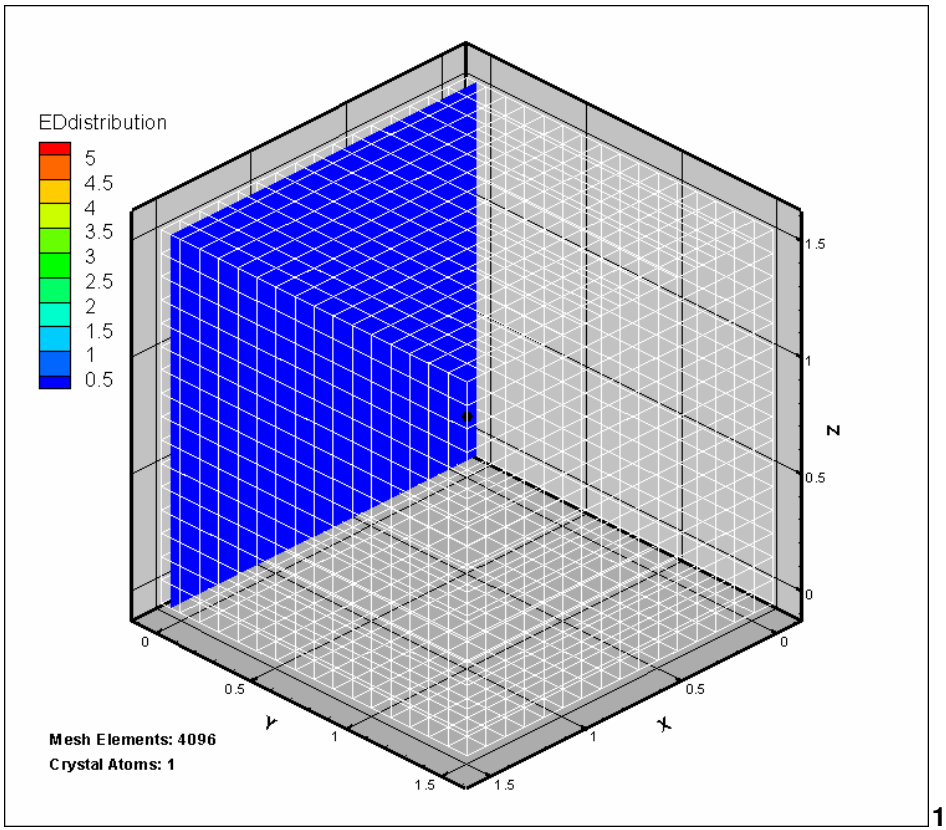
```
void evalFunctionGradient(double* pFunc, double* const pGrad);
double initial_value() const { return initialization_value; }
```

Interface to TAO



Post Processing





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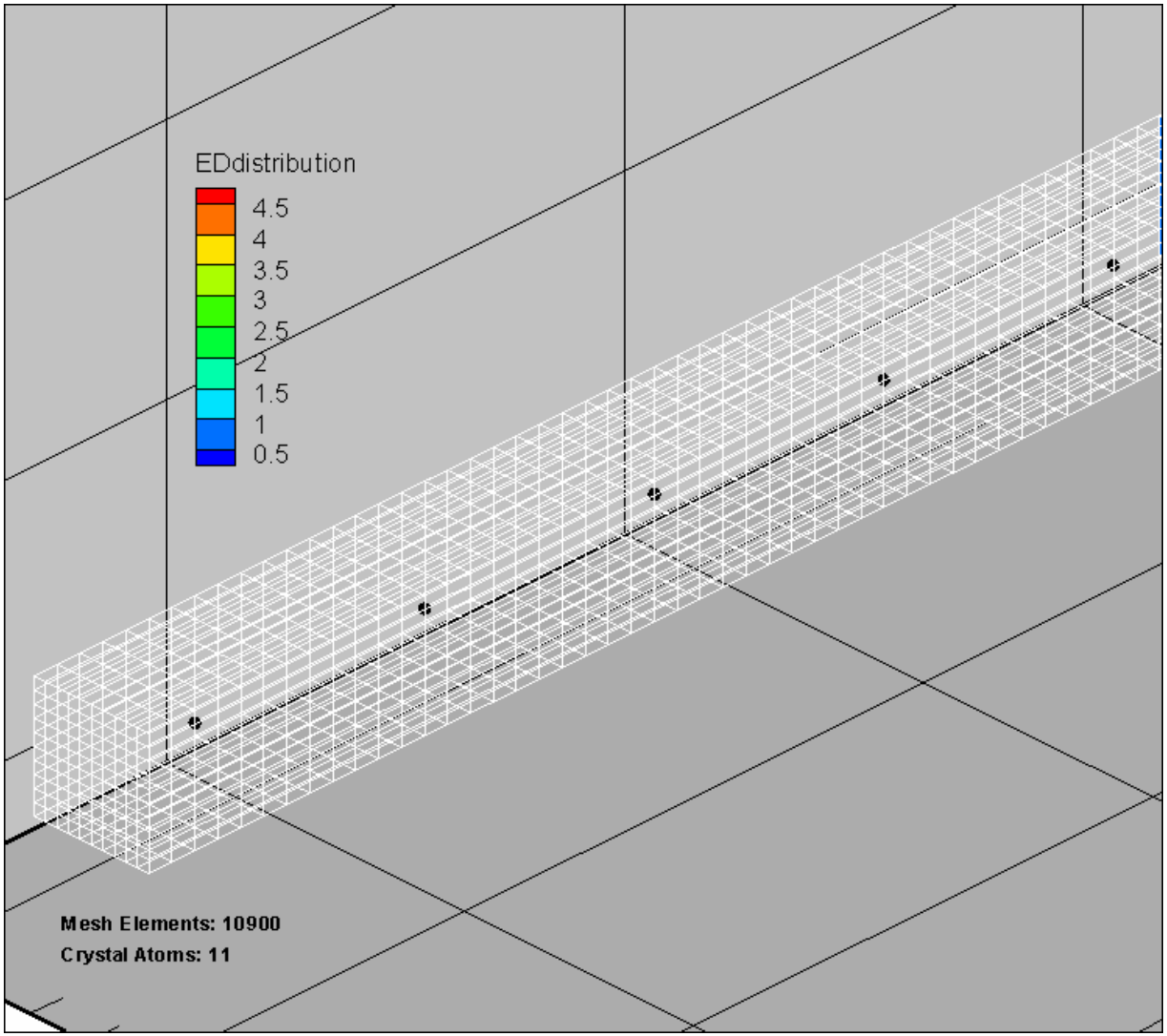

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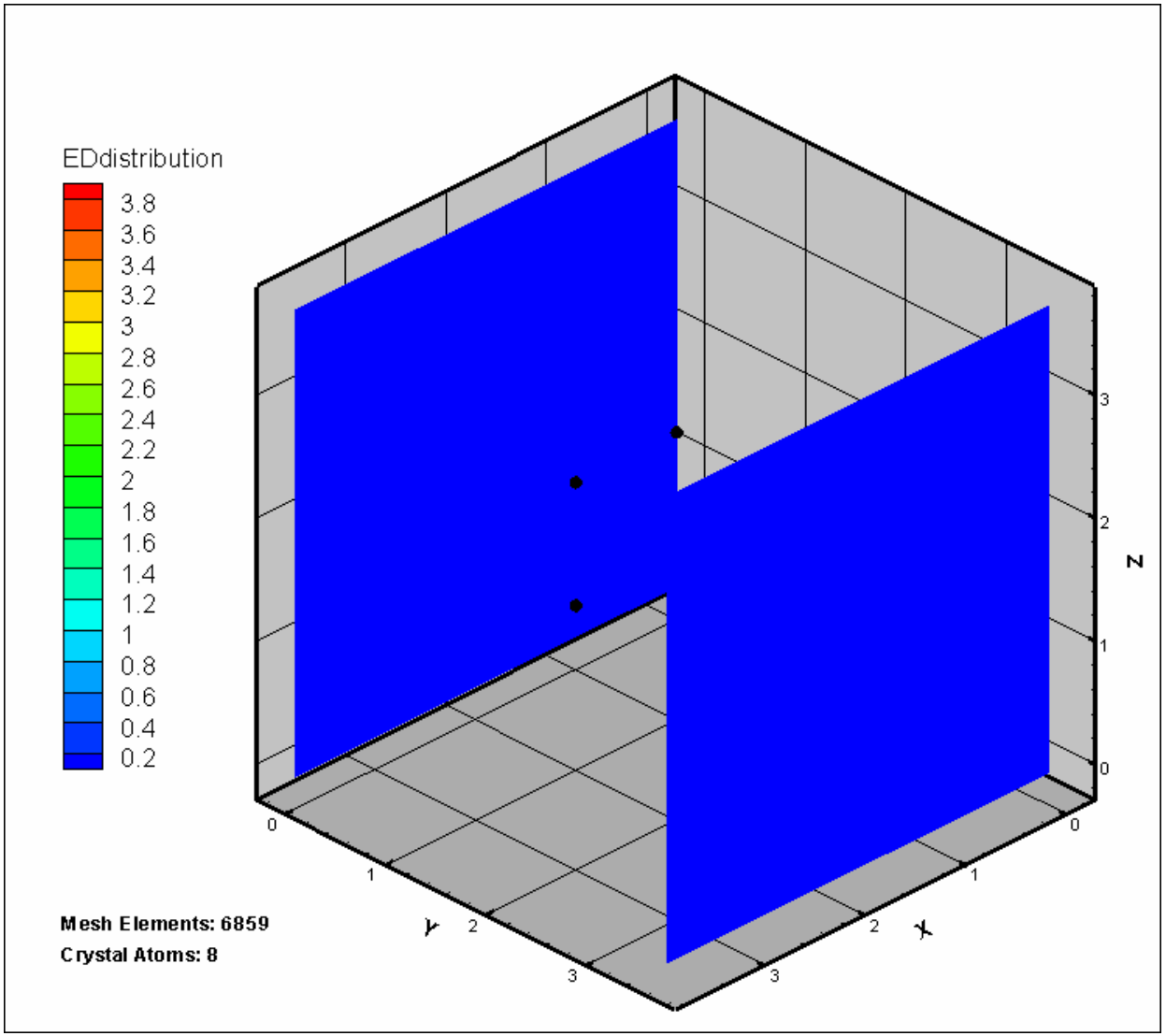

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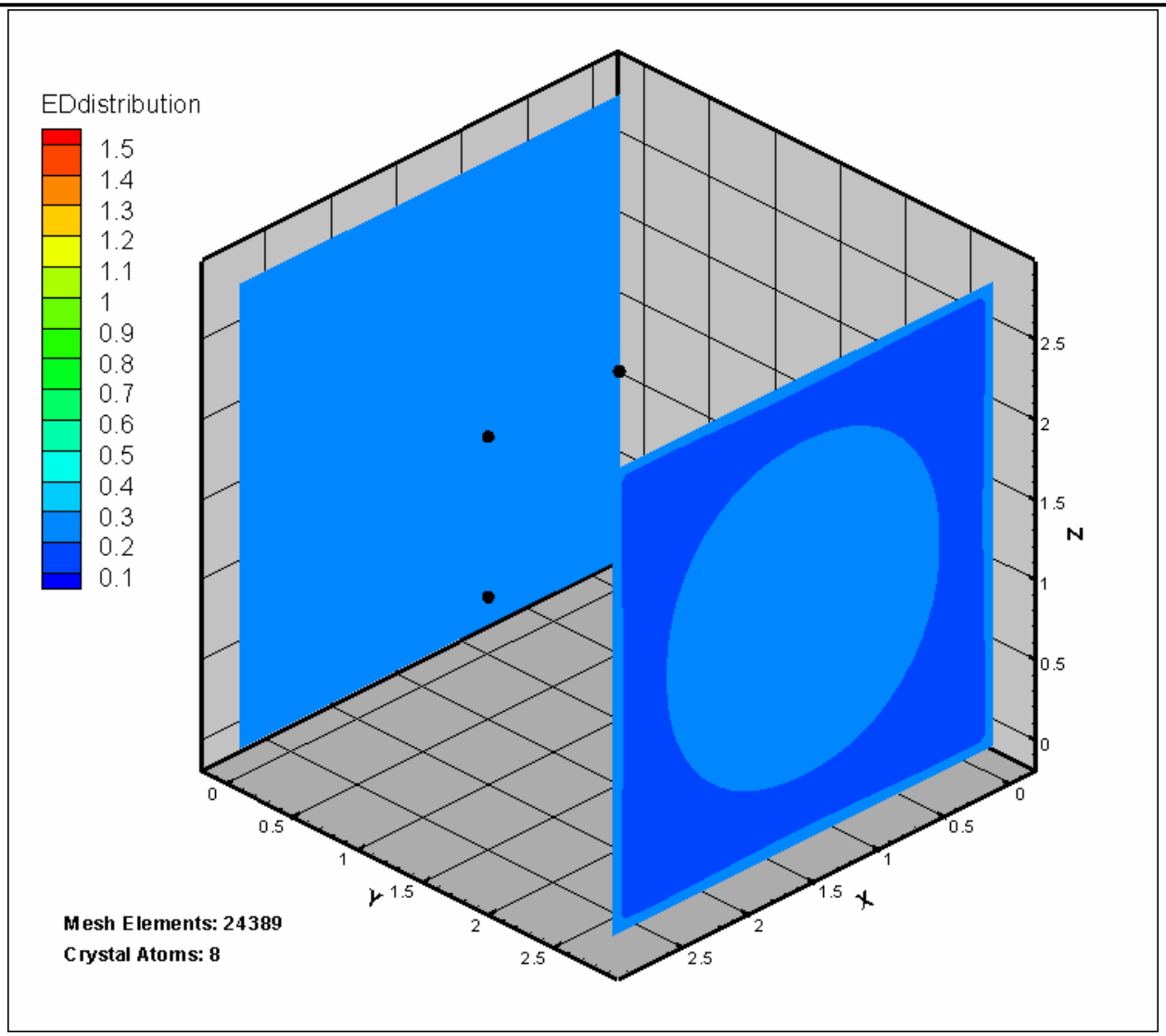

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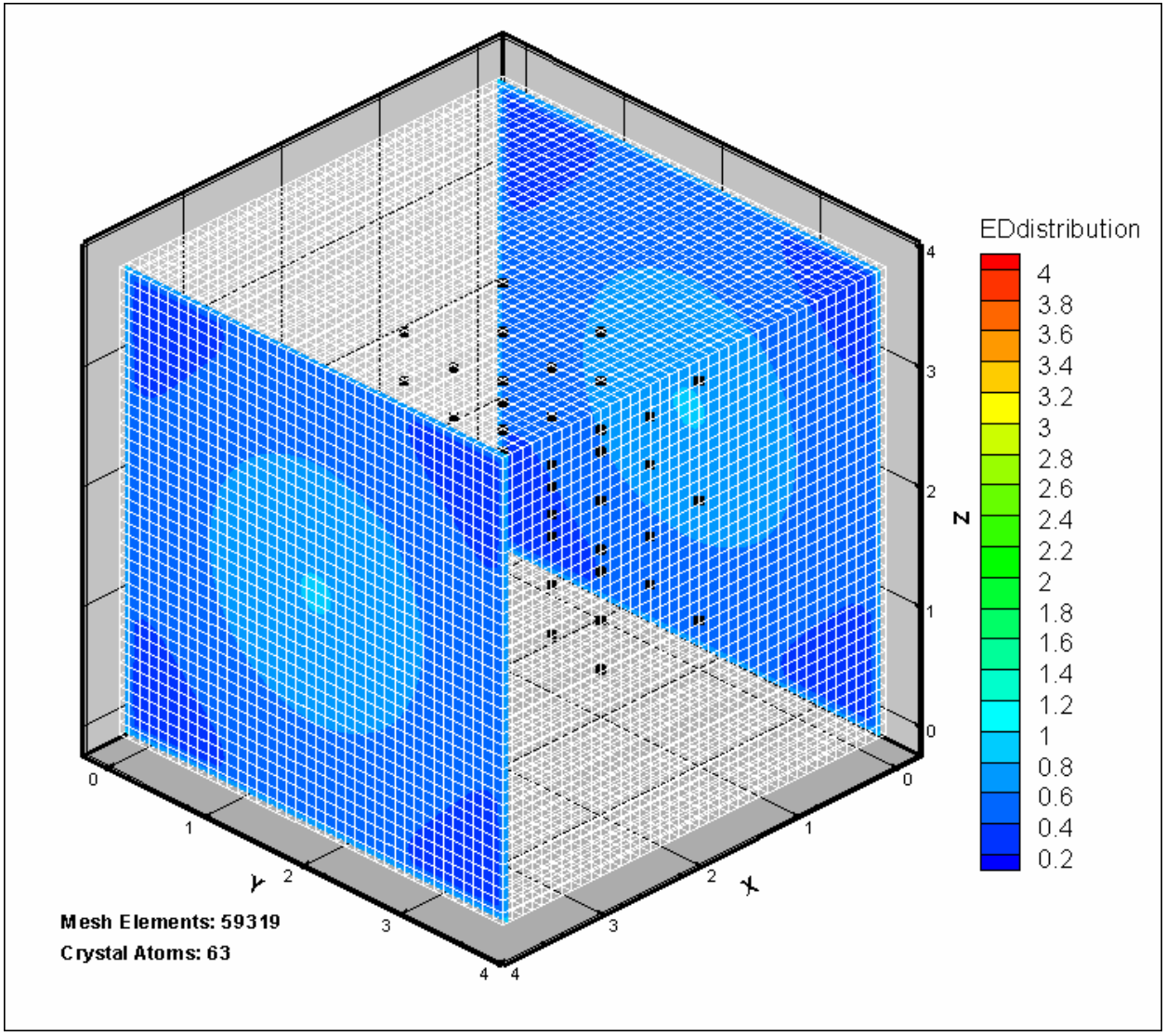
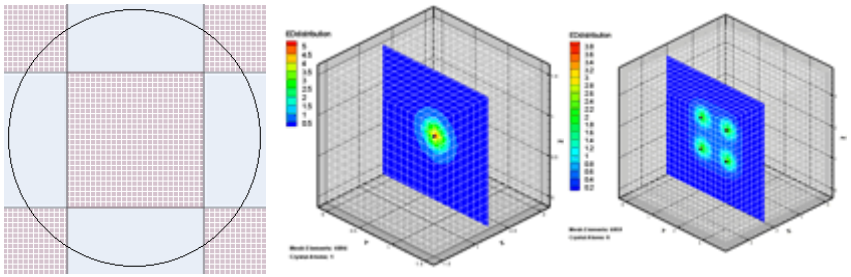
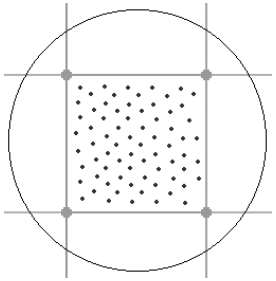


What's next …

- **Implement variable mesh size for the electron density computation [Electronic Problem]**



- **Implement an interface for use of different (higher order) shape functions [Ionic Problem]**



- **Parallelize the "function evaluation" using MPICH2 (both the model and the solution run in parallel at that point).**

Future work

- Significantly increase the dimension of the problem through a new algorithm
- Interface to third-party DFT computation packages (Peter Zapol – ANL, NWChem of PNNL)
- Looking into more sophisticated DFT models that are closer to physics
- Testing this methodology with real-life nanostructures
- Investigate applications in Mechanical Engineering and Biology

Thank you